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Mowrey, R.C.; McCormack, D.A.; Kroes, G.; Baerends, E.J.

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Vibrational de-excitation of $v=1$ H_2 during collisions with a Cu(100) surface

R. C. Mowrey
Theoretical Chemistry Section, Code 6189, Naval Research Laboratory, Washington, D.C. 20375-5342

D. A. McCormack and G. J. Kroes
Leiden Institute of Chemistry, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands

E. J. Baerends
Theoretical Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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The dynamics of vibrational de-excitation of $v=1$ H_2 on a Cu(100) surface is studied using a six-dimensional quantum wave packet method. The de-excitation probability increases with increasing collision energy and initial molecular rotational quantum number, j. A strong dependence on molecular orientation is found with molecules rotating with helicoptering motion ($m_j=j$) exhibiting larger de-excitation probabilities, in general, than those with cartwheeling motion ($m_j=0$). The final j-state distribution and quadrupole alignment are computed as functions of collision energy. The competition between vibrational de-excitation and other dynamic processes during the collision is analyzed. The total de-excitation probability is in good agreement with vibrational inelasticities from experiment but the calculations overestimate the population of scattered H_2 in $(v=0,j)$ for large j. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1359738]

I. INTRODUCTION

Advances in experimental techniques and theoretical methods are revealing increasingly detailed information about the dynamics of collisions of molecular hydrogen with metal surfaces. Much of the effort in this area focuses on understanding activated dissociative adsorption and its reverse process, associative desorption, for which H_2/Cu is a benchmark system. Analysis of the experimentally observed dependence of reaction probabilities on collision energy and initial quantum state, coupled with theoretical studies, provides insight into aspects of the molecular dynamics and the features of the potential energy surface (PES) affecting reactivity.

An analysis of early experimental measurements revealed that vibrationally excited H_2 is more reactive than ground state molecules.[1] This is consistent with a dissociation barrier located in the exit channel that results in a lower effective barrier height for vibrationally excited molecules due to a reduction in the vibrational energy along the reaction path.[2] Large probabilities for transitions between the ground and first excited vibrational state were observed for the Cu(111) (Refs. 3–5) surface. The collision energy at which vibrational excitation occurs coincides with the energy threshold for dissociation, suggesting that the two processes might occur on the same region of the potential energy surface.[3]

Quantum dynamics calculations demonstrated that vibrationally inelastic scattering is efficient for potential energy surfaces with a late barrier and large curvature, the same conditions that produce high reactivity for vibrationally excited molecules.[2,6] However, dynamics calculations treating reaction at a single surface site and using model potentials could not simultaneously reproduce the experimental value of the vibrational efficacy (the ratio of the difference between the energetic reaction thresholds for $v=1$ and $v=0$ and the vibrational quantum) and the coincidence of the vibrational excitation and reaction thresholds.[7] These results suggested that reaction and vibrational excitation occur at different surface sites, presumably the top site for vibrational excitation and the bridge site for reaction.[7,8]

This conclusion was supported by dynamics calculations using calculated (DFT) PES's for H_2 on Cu(100) using reduced-dimensional models to examine the dependence of reaction and vibrational excitation on the surface impact site.[9–12] Reactivity was highest at the bridge and hollow sites because they have the lowest energy barriers. Vibrational transitions occur readily during collisions at top sites because of the strong curvature of the reaction path in front of the barrier and its location far into the product channel.[9] Calculations modeling H_2 on Cu(100) that include all six molecular degrees of freedom for the initial states $v=0$, $j=0$,[13,14] $v=0$, $j=4$,[15,16] and $v=1$, $j=0$ (Ref. 14) predict large vibrational transition probabilities, in good agreement with experimental observations on other low index Cu surfaces.[3–5]

The present study focuses on the vibrational de-excitation of $v=1$ H_2 during collisions with Cu(100). A six-dimensional quantum wave-packet method was used to compute the dependence of the de-excitation probability on initial collision energy and rotational state for $j=0,1,2,3$. Molecular orientation effects and competition with other dynamic processes (e.g., reaction) account for the dependence of the probabilities on the initial rotational quantum numbers. The rotational-state distribution and orientational an-

isotropy of scattered molecules are explained in terms of features of the potential energy surface. Recent experimental advances, including the ability to overpopulate specific rovibrational states in molecular beams and to perform final-state population analysis,[17–19] offer the possibility for detailed state-to-state comparisons between the presented theoretical predictions and experimental observations yet to be performed. Some of the results we will present for the scattering of $(v=1, j=1)$ H_2 can be compared to existing experimental results. We suggest several experiments that could provide results to further test the accuracy of our calculations. The outline of the paper is as follows. The theoretical methods and computational details are described in Sec. II. Section III presents the results and discussion. Our conclusions are given in Sec. IV.

II. METHOD

The model problem consists of an H_2 molecule interacting with a static, corrugated Cu(100) surface. The Born–Oppenheimer approximation is assumed to hold and all electronic excitations are neglected. The Hamiltonian describing the motion of the H nuclei is a function of six coordinates and is given as

$$\hat{H}=-\frac{1}{2M}\left(\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right)-\frac{1}{2\mu}\frac{\partial^2}{\partial r^2}+\hat{H}_{\mathrm{rot}}+V(X,Y,Z,r,\theta,\varphi), \tag{1}$$

where M and μ are the total and reduced mass of H_2, respectively. Atomic units are used throughout this paper. The first term of Eq. (1) is the center-of-mass kinetic energy of the molecule with X, Y, and Z specifying the location of the center-of-mass of the molecule with respect to the surface. The second term in the Hamiltonian is the kinetic energy of the H_2 vibrational coordinate and r is the H–H separation distance. The third term describes the molecular rotational motion and V is the molecule–surface interaction potential. The orientation of the H–H bond is specified by θ and ϕ, the polar and azimuthal angles, respectively.

The interaction potential is a six-dimensional functional fit to the results of density functional theory (DFT) calculations performed using the Amsterdam BAND program.[20,21] Details of the DFT calculations and the fitting procedure used in constructing the potential are given in Ref. 22. One important difference in the potential used here with that of Ref. 22 is that an artificial well located above the bridge site was removed by shifting the range of Z (between 5 and $5.8a_0$ instead of 8.14 and $8.94a_0$) over which the potential shifts to its asymptotic value [Ref. 14(E)].

In these calculations we consider only collisions at normal incidence. This dramatically decreases the computational cost of the calculations because the symmetry of the surface permits a reduction in the size of the basis used to represent the wave function. The wave function, ψ, describing the H_2 nuclear motion is represented using the symmetry-adapted wave-packet (SAWP) method.[15,16,23,24] The SAWP method combines symmetry adapted rotation-diffraction basis functions, g, with a grid representation of normal translational and vibrational motion, f. The wave function is written as

$$\psi^{v_0 j_0 m_{j0}}(t)=\sum_{\Gamma j m_j \Gamma_d n m} f^{v_0 j_0 m_{j0}}_{\Gamma j m_j \Gamma_d n m} \times(Z,r,t) g_{\Gamma j m_j \Gamma_d n m}(X,Y,\vartheta,\varphi). \tag{2}$$

The overall symmetry species of the rotation-diffraction function is denoted by Γ and the symmetry of the diffraction function in g is labeled by Γ_d. The expansion includes only the symmetries Γ which are contained in the initial wave function describing the incident molecule with rovibrational quantum numbers v_0, j_0, and m_{j0}. Specific information for constructing the symmetry-adapted basis is available elsewhere for $m_j=0$,[23] m_j-even,[15] and m_j-odd initial states.[16]

The time propagation of the wave packet is evaluated using the absorbing boundary condition (ABC) evolution operator.[25] The ABC operator contains an optical potential that absorbs the wave packet at the edges of the grid corresponding to large values of Z and r. The initial wave packet is written as

$$\psi^{v_0 j_0 m_{j0}}=\varphi_{v_0 j_0}(r) g_{\Gamma j_0 m_{j0} A_1 00}(X,Y,\vartheta,\varphi) \times\int_{-\infty}^{\infty} dk' b(k')\frac{\exp(ik'Z)}{\sqrt{2\pi}}, \tag{3}$$

where

$$b(k)=\left(\frac{2\zeta^2}{\pi}\right)^{1/4}\{\exp[-(k_{\mathrm{av}}-k)^2\zeta^2+i(k_{\mathrm{av}}-k)Z_0] +\exp[-(k_{\mathrm{av}}-k)^2\zeta^2-i(k_{\mathrm{av}}-k)Z_0]\}. \tag{4}$$

The initial wave packet is a superposition of Gaussian functions in Z, with one moving toward the surface and the other moving away from the surface. The latter is absorbed by the optical potential. The initial vibrational function is $\varphi_{v_0 j_0}(r)$, ζ is a width parameter, k_{av} is the average translational momentum of the Gaussian components, and Z_0 is the location of the center of the Gaussian. Because the initial Gaussian is real, real operator algebra is used for the time propagation, which reduces the computational requirements of the calculations by about a factor of 2. An additional reduction in computer time and memory is achieved using a projection operator formalism to represent the initial rotation-diffraction channel on a separate, larger grid than is used for the other rotation-diffraction states.[26]

State-to-state transition probabilities are computed using a scattering amplitude formalism[27,28] in which the overlap of the wave function with H_2 gas-phase states is calculated at regular time intervals at a dividing surface, $Z=Z_\infty$, in the asymptotic region. A half-Fourier transform of the overlaps provides energy-dependent coefficients from which S-matrix elements are calculated. Reaction probabilities are computed by subtracting the cumulative probabilities for nonreactive scattering from unity.

The numerical details of the calculations are essentially the same as those used previously.[14,15] Results are presented for the $(v_0=1;\ j_0=0,1,2,3;\ m_{j0})$ initial states. Performing

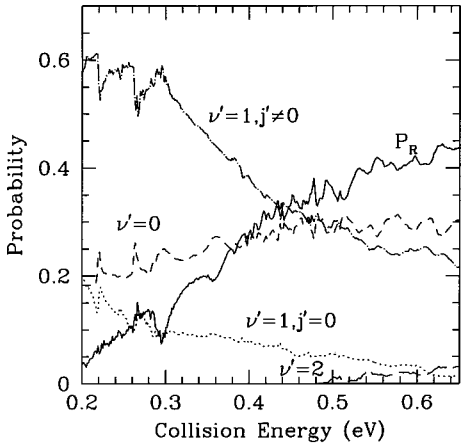

FIG. 1. Probabilities for survival (dotted line), vibrational de-excitation (short-dashed line), reaction (solid line), rotational excitation (dotted–dashed line), and vibrational excitation (long-dashed line) in scattering of $(v_0=1, j_0=0)$ H_2.

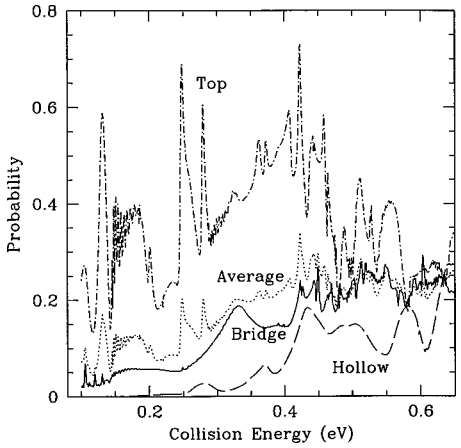

FIG. 2. Vibrational de-excitation probability for $(v_0=1, j_0=0)$ H_2 in fixed-site calculations for impact at bridge, hollow, and top sites and a site-weighted average.

separate calculations for low and high translational energies reduced the computational time of the calculations. Longer propagation times are required for low translational energies and larger basis expansions are required for high translational energies. Separating the calculations is more efficient than performing a single large-basis, long-propagation time calculation for each initial state. Low energy calculations typically require between 60 000 and 80 000 a.u. and high-energy calculations require 20 000–30 000 a.u. The rotational-diffraction basis used for low-energy calculations included $j \leqslant 24$ and $|n|+|m| \leqslant 11$ and the basis for high-energies included functions with $j \leqslant 29$ and $|n|+|m| \leqslant 14$.

III. RESULTS AND DISCUSSION

The probability for vibrational de-excitation from the $(v_0=1,\ j_0=0)$ state as a function of collision energy is shown in Fig. 1. For comparison, the probabilities for rotational excitation within the $v=1$ vibrational state, for reaction, for vibrational excitation (to $v=2$), and for no transition (referred to as survival) are shown. Although the focus of this paper is on vibrational de-excitation, a limited examination of some details of these additional processes is presented here because of the competitive role they play during a collision with the surface. The large vibrational de-excitation probability we compute (0.2–0.3) is in good agreement with the value of 0.28 determined from a fit to experimental observations for vibrational excitation of $(v_0=0)$ H_2 colliding with Cu(111) to the $(v=1,\ j=3)$ state.[5] Systems with large probabilities for vibrational excitation typically exhibit large probabilities for vibrational de-excitation because the processes are complementary. The predicted probability for vibrational de-excitation has only a moderate dependence on collision energy, rising from a value of 0.18 at 0.2 eV to 0.3 at 0.65 eV. This behavior is not surprising because the de-excitation process can, in principle, proceed using only the internal vibrational energy of the molecule (assuming that only moderate levels of rotational excitation accompany the de-excitation). A transition from the first excited-vibrational state to the ground vibrational state releases 0.504 eV of energy from the vibrational mode. Adding additional collision energy would not be expected to increase the effectiveness of the transition unless there is an energy barrier to overcome. The situation is quite different for reaction, vibrationally elastic rotationally inelastic scattering, and vibrational excitation. In each of these processes, the incident translational energy must be sufficient to cross the dissociation barrier (for reaction) or to excite internal vibrational or rotational modes. This is reflected in an increase in the probabilities for reaction and vibrational excitation to $v=2$ with increasing collision energy shown in Fig. 1. In contrast, the probabilities for vibrationally elastic rotational excitation and survival decrease with increasing collision energy because of the increasing importance of other competitive channels.

The results of 3D and 4D calculations, in which the position of the molecular center-of-mass is fixed above the high-symmetry bridge,[11] hollow, and top sites[12] are shown in Fig. 2. For collision energies below 0.46 eV the vibrational de-excitation probability is significantly larger for collisions at a top site than at bridge or hollow sites. In particular, at the lowest energies shown the probability of de-excitation at the top site is an order of magnitude larger than the value at the bridge site. The difference between the vibrational de-excitation probabilities at the top and bridge sites is not as large for collision energies between 0.46 and 0.65 eV. De-excitation probabilities for the top site vary from a low of about 0.13 to a high of 0.75 with an average value of about 0.4 for the collision energy range shown. The top site curve exhibits a great deal of structure, including sharp peaks previously identified as resonances associated with trapping at the surface as the intramolecular bond weakens and excitations to higher vibrational states occur.[9,10] At collision energies above 0.5 eV, the $v=2$ vibrational state (not shown) is energetically accessible and vibrational excitation competes with vibrational de-excitation, but this channel plays a minor role compared to reaction and rotational excitation.

Figure 2 shows the energy dependence for vibrational de-excitation obtained by averaging over the values obtained for the fixed-site models. The de-excitation probability is

about one-half the value obtained using the 6D model, shown in Fig. 1, at low energies but is almost the same at high energies. This agreement at high collision energies suggests that the relative probabilities for vibrational de-excitation at different surface sites shown in Fig. 2 should reflect the probabilities for de-excitation at the same sites in the 6D model calculations.

The domination of vibrational de-excitation by collisions at top sites is consistent with results obtained using a 2D model[9–12] to examine the scattering of ground state H_2 from Cu(100) which showed that reaction is more likely in collisions with bridge or hollow sites and vibrational excitation occurs primarily at the top site. Specifically, two-dimensional calculations[9,10] with the molecular axis held fixed parallel to the surface predict vibrational excitation probabilities of up to 40% for impact at a top site. In contrast, the same model predicts vibrational excitation probabilities of less than 1% for collisions at bridge and hollow sites and reaction probabilities approaching unity. This behavior results from the differing topography of the potential energy surfaces at the high symmetry sites (cf. Figs. 3 and 4 of Ref. 22). The dissociation barrier occurs at a large value of r for the top site because the molecular bond must lengthen to a greater extent than at other sites before the attractive forces associated with dissociation into the hollow or bridge sites overcome the Pauli repulsion due to electron overlap between the molecule and surface. Furthermore, at the top site the Pauli repulsion increases more rapidly as H_2 approaches the surface than is the case for the other sites because the molecule is directly over a surface atom. These features result in a potential energy surface with a late barrier and a high degree of curvature that causes efficient vibrational excitation[2] at the top site. Vibrational excitation occurs as translational energy of the incident molecule is shifted into the vibrational mode during the collision with the surface. This 2D model also predicts that the top site is efficient at causing vibrational de-excitation through the reverse procedure.

In a subsequent study the polar angle, θ, was included to develop a 3D fixed-site model for impact at the top and hollow sites and the polar and azimuthal angles, θ and φ, were added to construct a 4D model for the bridge site.[11,12] Calculations using these models predict that vibrational excitation occurs readily for collisions at top sites but predict significant, yet smaller, probabilities for vibrational excitation at the bridge site. Examination of the results revealed that vibrationally inelastic scattering can occur at the bridge site when the molecular axis is tilted in the range $60° < \theta < 80°$. For this orientation of the molecule, the PES has a large curvature and late barrier which are conducive to vibrational excitation. Values of $\theta > 80°$ lead primarily to dissociation at the bridge site but result in vibrational excitation at the top site. This explains why vibrational de-excitation probabilities are largest for collisions at the top site: at this site, vibrational de-excitation occurs over a wider range of molecular orientations, primarily because of the fact that dissociation is not as effective for molecules oriented with their axis parallel to the surface at the top site.

The dependence on collision energy of the averages of the parallel- and normal-translational and rotational energy of molecules that are vibrationally de-excited and those that are elastically scattered is shown in Fig. 3. The average rotational energy is an increasing function of collision energy for both elastically and inelastically scattered molecules, but the rotational energy is higher for the latter case at all collision energies. This is not unexpected because in addition to the incident collision energy, the vibrational energy released during de-excitation is available for transfer into other molecular modes (i.e., normal and parallel translation and rotation).

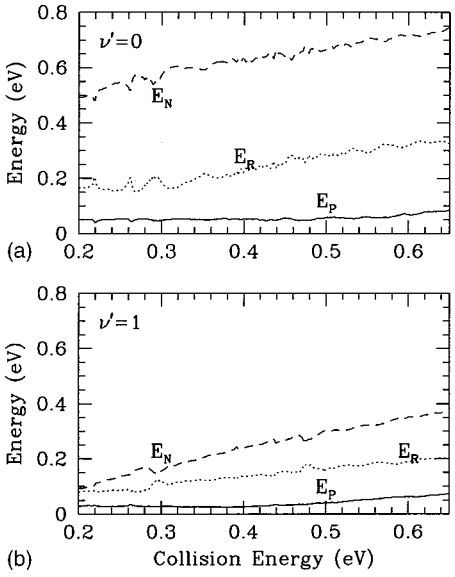

FIG. 3. Average values of normal translational energy (dashed line), parallel translational energy (solid line), and rotational energy (dotted line) for ($v_0=1, j_0=0$) H_2 scattered back in (a) $v'=0$ and (b) $v'=1$.

The diffraction energy is relatively constant for both elastically and inelastically scattered molecules. This independence from collision energy was seen for the average parallel translational energy for molecules incident in the ($v_0=0$, $j_0=0$) state[14] and in 4D calculations in which the molecular orientation was fixed parallel to the surface.[10] This result suggests that energy transfer into parallel translation is not governed by competition with rotational excitation or normal translation but rather by a dynamical restriction on the number of quanta of momentum transferred during a collision. The energy spacing between diffraction states is small so energy transfer into parallel translational motion saturates at low collision energies.

The average normal translational energy for vibrationally de-excited molecules is significantly larger than the energy in the other modes at all collision energies shown. At a collision energy of 0.2 eV, the final normal translational energy is slightly less than 0.5 eV (approximately the same value as the vibrational quantum for H_2) and the sum of the rotational and parallel translational energies is only 0.22 eV. This indicates that there is strong coupling by the PES of normal translational motion and molecular vibration that efficiently transfers energy between these modes. For collision energies above 0.3 eV the slope of the normal translation energy curve is only slightly larger than that of the rotational

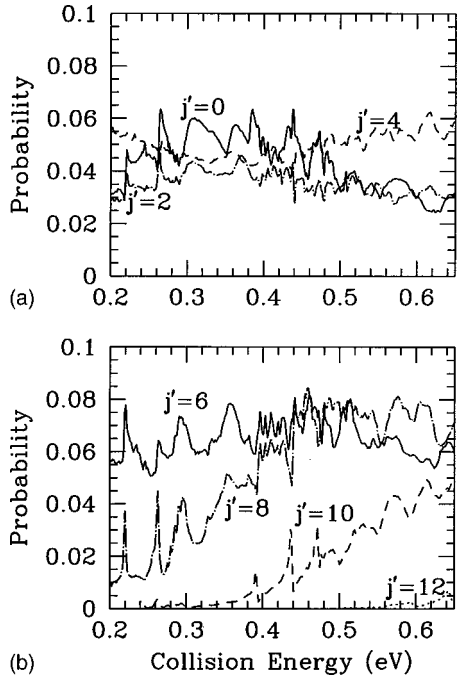

FIG. 4. Dependence of vibrational de-excitation probability on collision energy for $(v_0=1, j_0=0)$ H_2 for different final rotational states, j'.

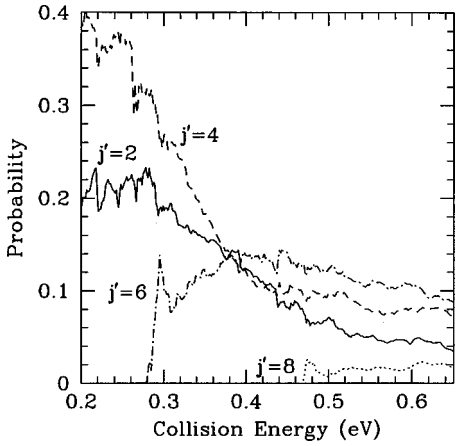

FIG. 5. Dependence of probabilities for vibrationally elastic, rotationally inelastic scattering for $(v_0=1, j_0=0)$ H_2 for different final rotational states, j'.

energy. This means that for each incremental increase in the collision energy above 0.3 eV, the additional energy is divided almost equally between rotation and normal translation of the reflected molecule.

Figure 4 shows the predicted vibrational de-excitation probabilities for different final rotational states, j', as a function of collision energy for $(v_0=1, j_0=0)$. Large changes in the rotational quantum number, j, can occur during vibrational de-excitation as is demonstrated by the significant probabilities for rotational states up to $j'=8$ throughout the energy range shown. The maximum probabilities predicted for all states with $j'<12$ are approximately the same and fall within the range ~0.05 to 0.08. After reaching the maximum value there is a gradual decrease in the de-excitation probability as the collision energy increases further (cf. $j'=0, 2$). It should be emphasized that there is no clear preference for excitation into a particular j' state but rather multiple states exhibit approximately the same probability for any given collision energy.

The asymptotic energy of the $(v'=0, j'=10)$ state is less than the total energy for collision energies above 0.22 eV. However, excitation into this state is negligible until 0.32 eV, where the probability increases and reaches a value of about 0.05 at a collision energy of 0.65 eV. The overall shape of the curve for $j'=10$ is characteristic of processes that involve crossing an energy barrier (cf., the reaction probability shown in Fig. 1). In comparison, the probabilities for vibrationally elastic, rotationally inelastic scattering into the $j'=6$ and 8 states, shown in Fig. 5, become nonzero when the collision energy exceeds the difference between the asymptotic energies of the final and initial states, 0.278 and 0.467 eV, respectively. The probabilities rapidly increase in magnitude, reaching a maximum value within a few hundredths of an eV. The source of the energy barrier for vibrational de-excitation to $j'=10$ is not apparent from an analysis of the computational results. One possibility is that the $(v=0, j=10)$ gas-phase rotational state correlates adiabatically with a highly excited librational state at the barrier, which cannot yet be populated at total energies just above that of the gas phase $(v=0, j=10)$ state.

For the purpose of providing a clear explanation, we consider the reverse scattering process: vibrational excitation of H_2 from $(v_0=0, j_0=10, m_{j0}=0)$ to $(v'=1, j'=0)$ during a collision at the top site. In the gas phase, the total energy of the incident molecule consists of the translational, rotational, and zero-point vibrational energies. As the molecule approaches the surface on the reaction path, the vibrational energy decreases as the molecular bond weakens. Rotational motion is no longer free but is hindered by the surface, eventually becoming libration for large internuclear distances. If the increase in the hindered rotation/libration energy exceeds the decrease in the vibrational energy, then the molecule will see an effective potential with a barrier that is higher than the energy of the gas-phase $(v=0, j=10)$ state. The collision energy must be large enough to enable the molecule to cross the effective barrier and move on to the region near the dissociation barrier for vibrational excitation to occur.

Vibrational de-excitation proceeds by the reverse process; the effective barrier height is the same in either case. The collision energy range in Fig. 4 is not low enough to confirm that this behavior (i.e., that the probability becomes nonnegligible at an energy somewhat greater than that at which the gas-phase state becomes energetically accessible) holds for $j'=8$. However, the rise in probability with increasing collision energy is similar to that for $j'=10$ which suggests that this is the case. Considering de-excitation into $(v'=0, j'=12)$, the probability remains small even though the collision energy is sufficiently large that this asymptotic channel is open.

Predicted probabilities for vibrational de-excitation from $(v_0=1, j_0=0)$ to m_j-resolved final states are shown in Fig. 6. For $j'=2$, the probabilities for scattering into the $m_j'=0$ state, in which the molecules tumble with a cartwheel-like motion, are larger than those for $m_j'=2$, which displays he-

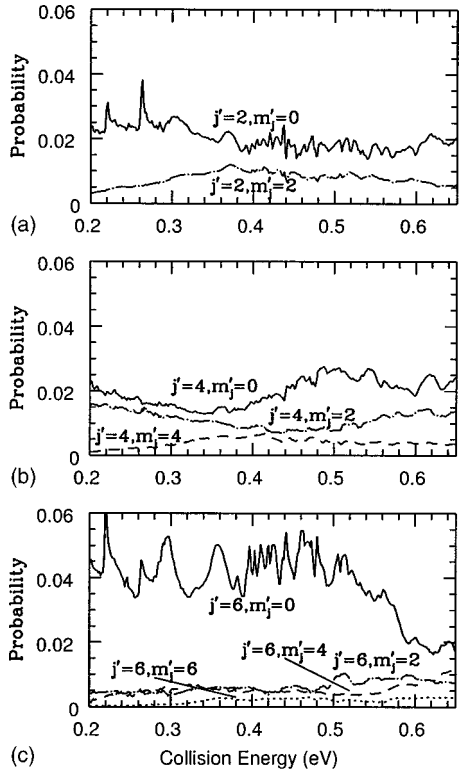

FIG. 6. Dependence of vibrational de-excitation probability on collision energy for ($v_0=1, j_0=0$) H_2 for particular final quantum states.

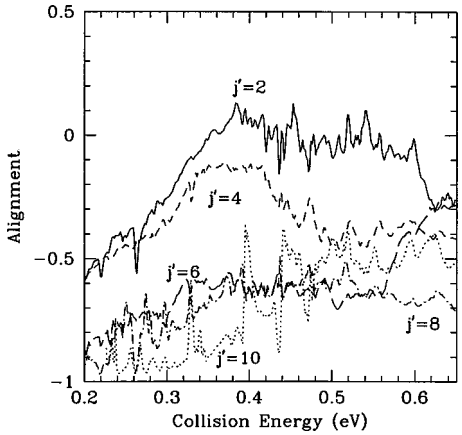

FIG. 7. Alignment of final $v'=0$ quantum states as a function of collision energy for ($v_0=1, j_0=0$) H_2.

licopterlike rotation. Note that the probability for $m_j'=1$ is equal to zero because the potential does not couple the even and odd states. The difference in probabilities between cartwheeling and helicoptering states is even larger for $j'=6$. Almost all molecules de-excited into this rotational state are oriented with their angular momentum vectors aligned parallel to the surface. Only at the highest collision energies shown does the sum of the probabilities of the $j'=6$, $m_j'=2,4,6$ states exceed that of $m_j'=0$. This preference for scattering into $m_j'=0$ for all j' states results from the fact that vibrational de-excitation occurs primarily for collisions at top sites, as was discussed previously. The PES used does not include azimuthal anisotropy at the top site so changes in the m_j quantum number are not possible for impact directly at the top site. Vibrational de-excitation involving m_j quantum number changes is a consequence of the azimuthal anisotropy of the PES at the bridge site. The fixed site results, shown in Fig. 2, predict small probabilities for vibrational de-excitation at the bridge site. Furthermore, the 6D PES uses an interpolation procedure to shift between the bridge and top sites. This means that the PES between these sites depends on φ to a varying degree and collisions impacting in this region can result in m_j transitions.

The m_j distribution of the scattered molecules is quantified by computing the quadrupole alignment,[29] which is given by

$$A_j^{(2)}(E)=\frac{\Sigma_{m_j}P'(E;j,m_j)[3m_j^2-j(j+1)]/j(j+1)}{\Sigma_{m_j}P'(E;j,m_j)}. \tag{5}$$

The alignment is equal to -1 when all the molecules have $m_j=0$ and is equal to zero when the distribution is isotropic. For $m_j=j$, the alignment has a positive j-dependent value that asymptotically approaches a value of 2 for increasing j. The alignment as a function of collision energy for final rotational quantum number, j, up to 10 is shown in Fig. 7 for $v'=0$. For $j=2,4$ the alignment is negative at low collision energies, increases to near zero at intermediate energies, and decreases at high collision energies. In contrast, for larger values of j the distribution remains polarized over the entire energy range examined, with most atoms scattering from the surface with cartwheel-type rotational motion. The fact that the computed alignments are mostly negative is consistent with most vibrational de-excitation occurring in the vicinity of the top site. The PES has weak anisotropy in phi near the top site, and therefore the probability that vibrational de-excitation will be accompanied by changes in m_j will be low and any changes in m_j that do occur will be small. As a result, the final m_j distributions will be nonstatistical and weighted towards low values of $|m_j'|$, and the higher j', the lower the alignment will be, as is also observed in our computational results.

In principle, it should be possible to experimentally determine whether the qualitative differences in the alignment for low and high values of j' are real. Results have been reported for the alignment of D_2 formed during associative desorption on Cu(111) as a function of the kinetic energy of the desorbing molecules.[30] Perhaps, the experimental configuration used in the associative desorption experiments can be modified to include an H_2 molecular beam, with the use of stimulated Raman pumping to overpopulate ($v=1, j=0$) in the incident molecular beam.[17–19] The stimulated Raman pumping technique has already been used in state-to-state molecular beam experiments measuring rovibrationally inelastic scattering from ($v=1, j=1$) to ($v'=0, j'$) states of H_2 on Pd(111) (Ref. 19) and on Cu(100) (Ref. 33, see also below), but the alignment of the backscattered molecules was not yet measured in these experiments. In principle, this can be done using linearly polarized light with resonance-enhanced multiphoton ionization (REMPI) as was done in Ref. 30. We are not aware of any reports describing experi-

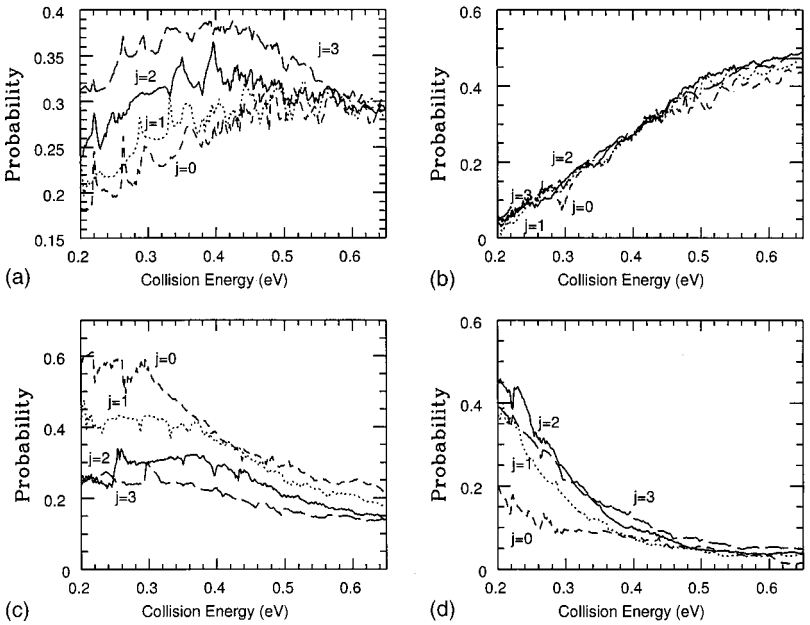

FIG. 8. Dependence of the probability for (a) vibrational de-excitation, (b) reaction, (c) vibrationally elastic rotationally inelastic scattering, and (d) survival on collision energy for statistical ($v_0=1$, $j_0=0,1,2,3$) H_2.

mental measurements of this type and it is possible that low signal intensities would mean that they are beyond current capabilities.

The probability for vibrational de-excitation of $v_0=1$ H_2 depends on the initial rotational quantum number, j_0, of the incident molecule as is shown in Fig. 8(a). The dependence of the vibrational de-excitation probability on collision energy is shown for statistical distributions of $j_0=0,1,2,3$ (m_j degeneracy averaged). Except for the highest collision energies examined, the probability for vibrational de-excitation increases with j_0, indicating that rotational energy enhances vibrational de-excitation. The effect is not purely energetic (i.e., with different energetic thresholds) because shifting the curves along the energy axis by the rotational energies of the initial states (0.014, 0.043, and 0.085 eV for $j=1,2,3$, respectively) does not make them coincident. At collision energies of 0.5 eV and higher the vibrational de-excitation probabilities from $j=0,1,2$ are approximately equal. Furthermore, above 0.45 eV the de-excitation probability from $j=3$ decreases with increasing collision energy and is the same magnitude as that for the other initial states at 0.55 eV. For each initial rotational state the de-excitation probability is not strongly dependent on collision energy, changing by about 0.1 over an energy range slightly smaller than the spacing between H_2 vibrational energy levels. The reduction in de-excitation probabilities at high collision energies is attributed to excitation to $v=2$ when that vibrational state becomes energetically accessible.

The reasons for the dependence of the vibrational de-excitation probability on j_0 become clearer by examining the probabilities for reaction, vibrationally elastic rotationally inelastic scattering, and survival for different initial states, shown in Fig. 8. An exhaustive analysis of these processes is beyond the scope of this study but an abbreviated discussion is appropriate because they compete with vibrational de-excitation and so affect its probability. In contrast to the vibrational de-excitation probability, which is dependent on the initial rotational quantum number, the degeneracy-averaged reaction probability, shown in Fig. 8(b), appears to be almost independent of j_0. As was mentioned previously, the m_j-resolved reaction probabilities differ for a particular initial j state, with molecules with helicoptering rotational motion having higher reactivity than cartwheeling molecules. However, averaging over the initial azimuthal quantum number for each rotational state produces an initially isotropic distribution of incident molecules so the fraction of cartwheeling and helicoptering molecules is the same for each initial j. The lack of dependence on j for the reaction probability indicates that rotational hindrance,[31,32] the increasing likelihood for molecules with high values of j to rotate into unfavorable geometries as they approach the barrier, is not a factor in the dissociation of $v=1$ H_2 on Cu(100). On the other hand, the lack of dependence on j also indicates that the rotational energy of the incident molecules does not couple to the reaction coordinate to aid in crossing the dissociation barrier.

For increasing initial j, the probability for vibrationally elastic, rotationally inelastic scattering decreases [Fig. 8(c)] and the survival probability (j does not change) increases [Fig. 8(d)]. This behavior is a consequence of two factors: (1) the conservation of m_j for collisions at the high-symmetry top and hollow sites, and (2) differences in the rotational anisotropy seen by the incident molecule depending on its orientation with respect to the surface. For the purposes of illustrating the differences in rotationally elastic scattering we will compare scattering of $j_0=0$ (nonrotating) and $j_0=2$ (rotating) molecules. The results for $j_0=1$ and 3 are similar to the latter. Considering first the case where $j_0=0$, for simplification we divide the initially isotropic distribution into two groups: molecules with their axis pointing approximately perpendicular to the surface and those with their axis approximately parallel to the surface. Molecules oriented with their axis perpendicular to the surface will experience a strong rotational anisotropy when colliding with the surface and large changes in j can result. For most collisions (i.e., at top and hollow sites) m_j will be conserved and

the molecules will scatter back with cartwheel-type rotational motion. Molecules incident with their axis parallel to the surface will experience a weaker rotational anisotropy and will be excited primarily to lower j rotational levels but again with cartwheeling rotational motion. For H_2 incident in $(j_0=2, m_{j0}=0)$ the molecule has cartwheel-type rotation, which leads to a strong repulsive interaction between the molecule and the surface when the molecular axis points into the surface, causing large probabilities for rotational transitions. The azimuthal quantum number is conserved in most collisions (top and hollow sites) so the scattered molecules retain their cartwheeling rotation except for some fraction of the molecules colliding at a bridge site.

For $(j_0=2, m_{j0}\neq 0)$ the plane of rotation is not perpendicular to the surface but is tilted. The anisotropy of the potential in θ seen by the molecule is less and results in smaller probabilities for rotationally inelastic scattering, particularly to large values of j. Probabilities involving rotational de-excitation to $(j=0, m_j=0)$ are not possible from $(j_0=2, m_{j0}=1)$ because the PES can couple only rotational states in which the azimuthal quantum numbers differ by a multiple of 2. Probabilities for rotational de-excitation from $(j_0=2, m_{j0}=2)$ to $(j=0, m_j=0)$ will be small because this can occur only at collisions at the bridge site. Even at the bridge site there is a tendency for transitions that conserve m_j to have larger probabilities than transitions in which m_j changes. Thus, molecules incident with $m_{j0}\neq 0$ have smaller probabilities for both rotational excitation and de-excitation resulting in less rotationally inelastic scattering than for $m_{j0}=0$ molecules. Averaging over the azimuthal quantum numbers results in lower rotationally inelastic probabilities for rotating molecules than for those that are not rotating.

The probabilities for rovibrationally elastic scattering (survival) from different initial j values are shown in Fig. 8(d). The survival probability for rotating molecules is larger than that for nonrotating molecules at low and moderate collision energies. This is mostly due to competition with vibrationally elastic, rotationally inelastic scattering, which is very efficient for $j=0$, but less efficient for $j>0$ [Fig. 8(c)]. We conclude by pointing out that the probabilities for reaction, vibrational de-excitation, and survival are almost independent of j at the highest collision energies examined. The probability for rotationally inelastic scattering decreases slightly with increasing j at high energies. The probabilities for vibrational excitation to $v'=2$ (not shown) increase with increasing j.

For $j_0>0$ the effect of changes in the initial azimuthal quantum number of the molecule on vibrational de-excitation can be examined. Figure 9 shows the dependence of the probability for vibrational de-excitation on m_j as a function of collision energy. Considering first the results for $j_0=1$ shown in Fig. 9(a), at low collision energies molecules with a helicoptering-type rotation have a larger de-excitation probability than those with cartwheeling-type rotation. For example, at a collision energy of 0.2 eV the de-excitation probabilities are 0.11 and 0.30 for $m_j=0$ and $m_j=1$, respectively. The probability increases with increasing collision energy for $m_j=0$ but does not change substantially for $m_j=1$, fluctuating around a value of about 0.32, in the latter

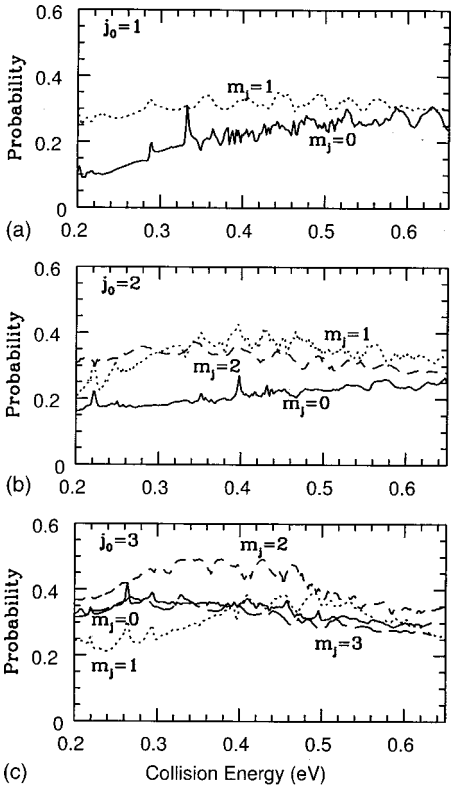

FIG. 9. Dependence of the vibrational de-excitation probability on collision energy and initial azimuthal quantum number for (a) $j_0=1$, (b) $j_0=2$, and (c) $j_0=3$.

case. At high collision energies the probabilities for the two initial azimuthal quantum numbers are comparable. The de-excitation probabilities for the $j_0=2$ rotational state manifold are shown in Fig. 9(b). As is the case for $j_0=1$, the de-excitation probability for molecules with cartwheeling rotational motion is smaller than that for helicoptering molecules. However, at a collision energy of 0.3 eV the probability for $m_j=1$ becomes larger than that for $m_j=2$. This is a consequence of differences in the competition between reaction and vibrational de-excitation for different m_j states. The symmetry of the potential energy surface results in a selection rule that prevents molecules with incident quantum numbers $j+m_j$ equal to an odd number from dissociating into two hydrogen molecules in the H-surface vibrational ground state. This means that the effective dissociation barrier is higher and, consequently, the reaction probability is lower for the $m_j=1$ state than for $m_j=0,2$. Thus a larger fraction of the molecules incident in $m_j=1$ scatter back to the gas phase than for $m_j=2$ and many of these surviving molecules undergo vibrational de-excitation. The vibrational de-excitation probability for $m_j=0$ remains smaller than for the other states shown primarily because of increased competition with rotationally inelastic scattering, in which v is conserved (not shown here). Figure 9(c) shows the de-excitation probabilities for $j_0=3$. The de-excitation probability for $m_j=3$ (helicoptering rotation) is never the largest because reaction is a more effective competitive process for this incident state than it is for the other m_j states. The de-excitation probability for $m_j=0$ (cartwheeling rotation) is

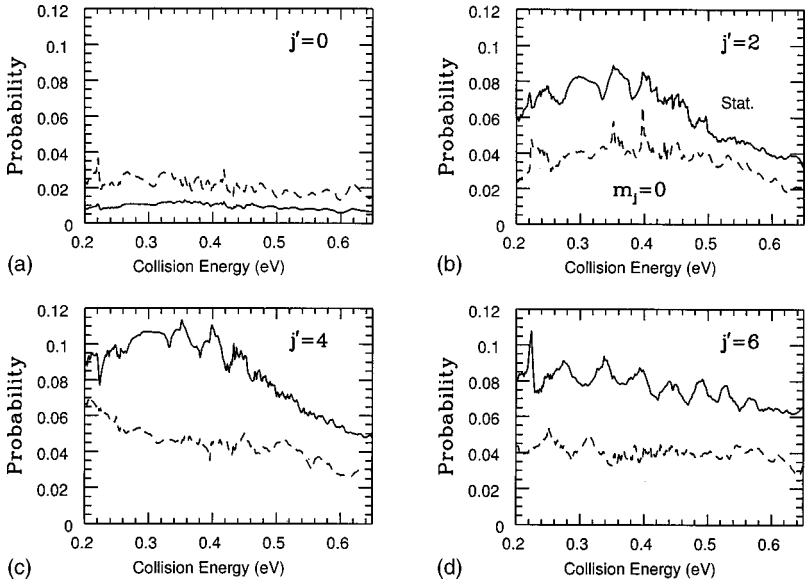

FIG. 10. The dependence of the final rotational state resolved vibrational de-excitation probability on collision energy is shown, for statistical $(v_0=1, j_0=2)$ H_2 (solid line) and for cartwheeling $(v_0=1, j_0=2, m_{j0}=0)$ (dashed line), for different final rotational states, j': (a) $j'=0$, (b) $j'=2$, (c) $j'=4$, (d) $j'=6$.

larger than that for $m_j=1$ at low collision energies because of large reaction probabilities for the latter state.

The final rotational state resolved vibrational de-excitation probabilities for statistical $(v_0=1, j_0=2)$ and cartwheeling $(v_0=1, j_0=2, m_{j0}=0)$ H_2 are shown in Fig. 10. The results for $j_0=1$ and 3 are similar so they are not shown. As is the case for the $j_0=0$ initial rotational state (Fig. 4), the probabilities for excitation to high values of j are large. This is a consequence of the strong rotational anisotropy of the potential energy surface near the surface. The probabilities for rotational de-excitation to $(v'=0, j'=0)$ are smaller than those of any of the other final states shown, with average values of about 0.01 and 0.02 for statistical and cartwheeling rotational motion, respectively. The probabilities for $j'=0$ show little dependence on collision energy aside from small magnitude fluctuations. Probabilities for vibrational de-excitation of both cartwheeling and statistical H_2 to $j'=2,4,6$ are larger than those for $j'=0$ throughout the energy range shown.

Comparing the probabilities for scattering into a particular final rotational state, j', for molecules incident with cartwheeling rotational motion $(m_j=0)$ or for a degeneracy-averaged distribution shows that, with the exception of $j'=0$, the statistical distribution produces higher de-excitation probabilities. This occurs because molecules with the molecular axis approximately parallel to the surface $(m_j \approx j)$ have an optimal orientation for vibrational de-excitation but those with the axis perpendicular to the surface, which is the case at least part of the time for $m_j=0$, are less likely to vibrationally de-excite. Thus the de-excitation probabilities for initial $m_{j0}=1$ or 2 (not shown) are larger than those for $m_{j0}=0$ for each value of j'. The vibrational de-excitation probability to $j'=0$ for cartwheeling molecules is larger than that for a statistical distribution because the potential energy surface does not couple the $(j=2, m_j=1)$ and $j=0$ states and, as a consequence, the average over initial m_j states is lowered.

The large probabilities for vibrationally inelastic rotational transitions to large-j states (Figs. 4 and 10) are not consistent with recent state-to-state measurements for scattering of $(v_0=1, j_0=1)$ H_2 from Cu(100).[33] Stimulated Raman pumping was used to overpopulate $(v_0=1, j_0=1)$ in the incident molecular beam. The population of selected final states was measured using resonance enhanced multiphoton ionization. At a collision energy of 74 meV the probabilities for $(v'=0, j'=5)$ and $(v'=0, j'=7)$ are 0.009 and 0.0005, respectively. The predicted probabilities are 0.09 and 0.01, respectively, at 100 meV, the lower energy limit used in our calculations. It seems unlikely that the computed probabilities will decrease by an order of magnitude for the lower collision energy used in the experiments. The computed probabilities for $(v'=0, j'=1)$ and $(v'=0, j'=3)$ are 0.025 and 0.05, respectively. The population in these states has not been measured experimentally because of complications caused by their presence as major components in the incident molecular beam. The experimental and computed probabilities for survival in $(v'=1, j'=1)$ are in good agreement with values of 0.46 and 0.5, respectively. The experimental probabilities for rotationally inelastic scattering to $(v'=1, j'=3)$ for a collision energy of 0.11 eV is 0.017, more than an order of magnitude smaller than the computed value of 0.35 at the same collision energy. The calculations predict a probability of 0.2 for scattering into $(v'=1, j'=5)$ at collision energies near 0.2 eV but no scattered molecules were detected in this state in the experiment. These results indicate that although the present computational model correctly predicts the survival probability, it overestimates the amount of rotationally inelastic scattering for both vibrationally inelastic and elastic scattering.

This conclusion is supported by a recent, but more limited set of quantum wave-packet calculations [only the $(v_0=1, j_0=1)$ initial state was considered] on H_2 scattering from Cu(100),[33] using a new potential energy surface (PES IV) (Ref. 34) based on an expansion to fourth-order in spherical harmonics at all high-symmetry sites. This PES includes the azimuthal dependence on the molecular orientation at the top and hollow sites. Furthermore, the higher-order expansion reduces the anisotropy of the potential in θ,

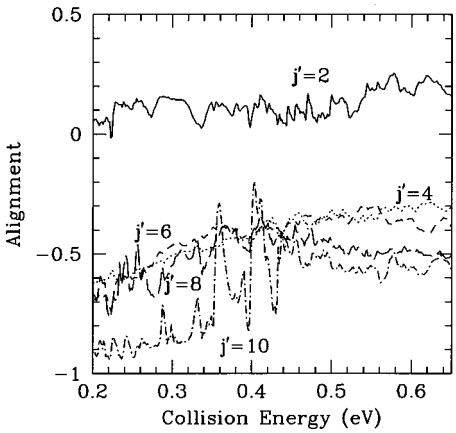

FIG. 11. Alignment of final $v'=0$ quantum states as a function of collision energy for statistical ($v_0=1, j_0=2$) H_2.

which reduces the probabilities for large rotational transitions. Specifically, for a collision energy of 0.1 eV the probabilities for vibrational de-excitation into $(v'=0, j'=1)$ and $(v'=0, j'=3)$ using PES IV are twice as large as those obtained using PES III. The probability for $(v'=0, j'=5)$ is similar for both potentials but transitions into $j'>5$ have significantly smaller probabilities for PES IV. Similar reductions in the degree of rotationally inelastic scattering are seen for $v'=1$. The survival probability is about the same for each PES.

We note first of all that results obtained using PES IV are in better agreement with experiment than those obtained using PES III because of a decrease in the fraction of scattered molecules excited to high rotational states. This is true for both vibrationally elastic and inelastic scattering. Second, the amount of vibrationally inelastic scattering increases using PES IV primarily because of an increase to 0.17 of the population of molecules scattered in $(v'=0, j'=1)$ and $(v'=0, j'=3)$, compared to a population of 0.075 in the same states for PES III. In the experiments, a large fraction ($\sim$0.5) of the incident molecules are unaccounted for in the scattered beam and are presumed to either react or scatter in one of these unobserved, low j channels.[33] Calculations using PES III and IV (Ref. 33) as well as an analysis of experiments[1] indicate that the reaction probability should be negligible at 0.1 eV. This leaves the low j states of $v=0$ as the most likely place to find the unobserved scattered molecules. The populations of these states predicted by the calculations are below the upper limits set by the fraction of the unobserved molecules. The improvement in the agreement between experiment and theory with PES IV is encouraging. It suggests that a more accurate description of the angular dependence of the PES is necessary, a possibility that will be explored in future studies. It is hoped that further experimental work will provide values for the populations of molecules scattered into the low $(v'=0, j')$ states.

The dependence on collision energy of the alignment of backscattered H_2, for H_2 initially incident in the $(v_0=1, j_0=2)$ state, is shown in Fig. 11. The alignment is positive for all collision energies for $j'=2$ but negative for all other final rotational states. The underlying reason for these values for the alignment is a propensity for m_j conservation in the scattering process. As was stated previously, the potential energy surface used in these calculations does not depend on the azimuthal angle when the molecule is located above the top or hollow sites because of the use of a low-order spherical harmonic expansion to represent the PES. The largest probabilities for vibrational de-excitation are found for collisions with a top site, particularly for low collision energies, which means that in most collisions leading to vibrational de-excitation the azimuthal quantum number of the scattered molecule remains the same as its initial value. For final states $j'\geqslant 4$ this will result in negative alignments (as seen in Fig. 11), due to small probabilities for final states with $m_j>2$ because of the absence of molecules with such values of m_j in the incident beam, for $j_0=2$. Another trend noted in the discussion of Fig. 10 is that probabilities for scattering into final states $(v'=0, j'\neq 0)$ are larger for molecules in the initial states $m_j=1$ and 2 (helicoptering) than for $m_j=0$ (cartwheeling). This trend is reflected in the population of scattered molecules in the final states $(v'=0; j'=2; m_j'=1,2)$ being larger than the population in $(v'=0, j'=2, m_j=0)$ which accounts for the positive value of the alignment for $j'=2$.

Figure 11 shows that there is a general trend for the alignment for $j'\geqslant 4$ to become less negative as the collision energy increases. This is a consequence of vibrational de-excitation at the bridge site becoming significant relative to that at the top site at higher collision energies. Changes in the azimuthal quantum number are possible for collisions at the bridge site so the fraction of the population in higher m_j states is larger which increases the value of the alignment. Although it is now possible to experimentally determine the relative probabilities for vibrational de-excitation by measuring the populations of scattered molecules in particular final j states,[17] no measurements of the alignment of the scattered molecules have yet been reported. Such results would be of considerable interest, particularly if significant differences are seen in the alignments for $j'=j_0$ and $j'\geqslant j_0$ as is predicted by these calculations. The current calculations suggest that the energy dependence of the alignment might be indicative of the relative importance of individual surface sites for vibrational de-excitation. An increase in the value of the alignment for states with $j'\geqslant j_0$ is consistent with an increase in probability for vibrational de-excitation at the bridge site. The overall value of the alignment is an indicator of the azimuthal corrugation of the surface. Negative alignments of large magnitude for states with $j'\geqslant j_0$ indicate that the surface has little azimuthal corrugation.

IV. CONCLUSIONS

Results of a computational study of vibrational de-excitation of H_2 from $v_0=1$ during collisions with a Cu(100) surface were presented. The quantum mechanical model, which includes all six molecular degrees-of-freedom, provides a reasonable description of the competition between vibrational de-excitation, other rovibrational transitions, and reaction with the surface. The computed quantum-state-resolved probabilities provide a more detailed picture of the

dynamics of vibrational de-excitation during collisions with surfaces than has been available previously. Where possible, the computational results are compared with experimental measurements as a test of the accuracy of the model. Additional predictions are offered to suggest possible experiments that would shed light on the vibrational de-excitation process and the general features of the H_2/Cu(100) potential energy surface.

The predicted degeneracy-averaged vibrational de-excitation probabilities are substantial for the initial rotational states and collision energies examined, in agreement with experimental measurements of vibrational excitation probabilities on other low-index faces of copper. The vibrational de-excitation probability is strongly dependent on the rotational quantum numbers and collision energy of the incident molecule. In particular, the vibrational de-excitation probabilities for $j_0=0$ and $j_0=3$ differ by almost a factor of 2 at a collision energy of 0.2 eV but are comparable at 0.65 eV.

As is the case for reaction with the surface, molecules incident with helicoptering rotational motion are more likely to be vibrationally de-excited, in general, than molecules with cartwheeling rotational motion. This behavior should produce observable differences in the final-j state resolved de-excitation probabilities for incident beams with statistical and cartwheeling rotational motion.

Fixed-site calculations show that the largest probabilities for vibrational de-excitation occur for collisions near the top site of the surface, followed by the bridge and hollow sites. The absence of anisotropy in ϕ at the top site (and of less significance, at the hollow site) means that the azimuthal quantum number is conserved during most collisions involving vibrational transitions. As a consequence, the rotational alignment of vibrationally de-excited H_2 should be negative for final rotational states with large values of j', indicating that de-excited molecules scatter predominately with cartwheeling rotational motion. This is a prediction that has yet to be confirmed experimentally.

A comparison of predicted initial and final j-resolved probabilities with recent experimental results for H_2 on Cu(100) indicates that the calculations overestimate the amount of rotationally inelastic scattering that occurs for both vibrationally elastic and inelastic transitions. This is probably a consequence of truncating the spherical harmonic expansion of the potential energy surface at second order, which makes the potential too anisotropic in the polar angle. Calculations using a similar PES but with a fourth-order spherical harmonic expansion[33] report a shift of probability from high final j to low j states, toward better agreement with experiment, which supports this assertion.

Experiments measuring the probabilities for scattering into $(v'=0,j')$ for low values of j' would provide important, but missing, information on the importance of vibrational transitions that do not involve large rotational changes. Further computational work using alternative forms for the PES is planned.

Analysis of the average energy of de-excited molecules reveals that more energy is concentrated in normal translational motion (>0.5 eV) than in rotational and parallel translational motion combined. This is a consequence of the efficient coupling of normal translation and vibration by the potential energy surface at the top site, the surface site with the largest probabilities for vibrational state transitions. Rotational excitation accompanies vibrational de-excitation, with rotational states up to $j=10$ showing significant probabilities. There is not a single final rotational state with a substantially larger population than any other, but rather, for any particular collision energy several states have approximately the same probability. The probability for de-excitation into higher rotational states (e.g., $j'=10$) does not become nonzero until well after the total energy exceeds the energy required to access the gas-phase asymptotic state.

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[1] H. A. Michelsen and D. J. Auerbach, J. Chem. Phys. **94**, 7502 (1991).
[2] D. Halstead and S. Holloway, J. Chem. Phys. **93**, 2859 (1990).
[3] C. T. Rettner, D. J. Auerbach, and H. A. Michelsen, Phys. Rev. Lett. **68**, 2547 (1992).
[4] A. Hodgson, J. Moryl, P. Traversaro, and H. Zhao, Nature (London) **356**, 501 (1992).
[5] C. T. Rettner, H. A. Michelsen, and D. J. Auerbach, Chem. Phys. **175**, 157 (1993).
[6] G. R. Darling and S. Holloway, J. Chem. Phys. **97**, 734 (1992).
[7] G. R. Darling and S. Holloway, Surf. Sci. **307–309**, 153 (1994).
[8] G. R. Darling and S. Holloway, Rep. Prog. Phys. **58**, 1595 (1995).
[9] G. J. Kroes, G. Wiesenekker, E. J. Baerends, and R. C. Mowrey, Phys. Rev. B **53**, 10397 (1996).
[10] G. J. Kroes, G. Wiesenekker, E. J. Baerends, R. C. Mowrey, and D. Neuhauser, J. Chem. Phys. **105**, 5979 (1996).
[11] R. C. Mowrey, G. J. Kroes, G. Wiesenekker, and E. J. Baerends, J. Chem. Phys. **106**, 4248 (1997); **110**, 2740(E) (1999).
[12] R. C. Mowrey, G. J. Kroes, and E. J. Baerends, J. Chem. Phys. **108**, 6906 (1998).
[13] G. J. Kroes, E. J. Baerends, and R. C. Mowrey, Phys. Rev. Lett. **78**, 3583 (1997); **81**, 4781(E) (1998).
[14] G. J. Kroes, E. J. Baerends, and R. C. Mowrey, J. Chem. Phys. **107**, 3309 (1997); **110**, 2738(E) (1999).
[15] D. A. McCormack, G. J. Kroes, E. J. Baerends, and R. C. Mowrey, Faraday Discuss. **110**, 267 (1998).
[16] D. A. McCormack, G. J. Kroes, R. A. Olsen, E. J. Baerends, and R. C. Mowrey, J. Chem. Phys. **110**, 7008 (1999).
[17] M. Gostein, H. Parhikhteh, and G. O. Sitz, Phys. Rev. Lett. **75**, 342 (1995).
[18] A. Hodgson, P. Samson, A. Wight, and C. Cottrell, Phys. Rev. Lett. **78**, 963 (1997).
[19] M. Gostein, E. Watts, and G. O. Sitz, Phys. Rev. Lett. **79**, 2891 (1997).
[20] G. te Velde and E. J. Baerends, Phys. Rev. B **44**, 7888 (1991).
[21] G. te Velde and E. J. Baerends, J. Comput. Phys. **99**, 84 (1992).
[22] G. Wiesenekker, G. J. Kroes, and E. J. Baerends, J. Chem. Phys. **104**, 7344 (1996).
[23] G. J. Kroes, J. G. Snijders, and R. C. Mowrey, J. Chem. Phys. **102**, 5512 (1995).
[24] G. J. Kroes, J. G. Snijders, and R. C. Mowrey, J. Chem. Phys. **103**, 5121 (1995).
[25] V. A. Mandelshtam and H. S. Taylor, J. Chem. Phys. **103**, 2903 (1995).
[26] D. Neuhauser and M. Baer, J. Chem. Phys. **91**, 4651 (1989).
[27] G. G. Balint-Kurti, R. N. Dixon, and C. C. Marston, J. Chem. Soc., Faraday Trans. **86**, 1741 (1990); Int. Rev. Phys. Chem. **11**, 317 (1992).
[28] R. C. Mowrey and G. J. Kroes, J. Chem. Phys. **103**, 1216 (1995).
[29] R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).

[30] H. Hou, S. J. Gulding, C. T. Rettner, A. M. Wodtke, and D. J. Auerbach, Science **277**, 80 (1997).
[31] G. R. Darling and S. Holloway, Faraday Discuss. **96**, 43 (1993).
[32] G. R. Darling and S. Holloway, J. Chem. Phys. **101**, 3268 (1994).
[33] E. Watts, G. O. Sitz, D. A. McCormack, G. J. Kroes, R. A. Olsen, J. A. Groeneveld, J. N. P. van Stralen, E. J. Baerends, and R. C. Mowrey, J. Chem. Phys. **114**, 495 (2001).
[34] D. A. McCormack, G. J. Kroes, R. A. Olsen, J. A. Groeneveld, J. N. P. van Stralen, E. J. Baerends, and R. C. Mowrey, Faraday Discuss. **117**, 109 (2000).